

MODIFICATION OF BASE-SIDE ^{99}Mo PRODUCTION PROCESSES FOR LEU METAL-FOIL TARGETS

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ABSTRACT

Argonne National Laboratory is cooperating with the National Atomic Energy Commission of the Argentine Republic (CNEA) to convert their ^{99}Mo production process, which uses high enriched uranium (HEU), to low-enriched uranium (LEU). The program is multifaceted; however, discussed in this paper are (1) results of laboratory experiments to develop means for substituting LEU metal-foil targets into the current process and (2) preparation of uranium-alloy or uranium-metal/aluminum-dispersion targets. Although ^{99}Mo production is a multi-step process, the first two steps (target dissolution and primary molybdenum recovery) are by far the most important in the conversion. Commonly, once molybdenum is separated from the bulk of the uranium, the remainder of the process need not be modified. Our results show that, up to this point in our study, conversion of the CNEA process to LEU appears viable.

INTRODUCTION

A number of current producers dissolve uranium-aluminide/aluminum-dispersion plates in alkaline solution as an initial step to recovering fission-product ^{99}Mo from irradiated high-enriched uranium (HEU). These producers include Argentine Comisión Nacional de Energía Atómica (CNEA), Institut National des Radioéléments (IRE), Mallinckrodt, and the Atomic Energy Corporation of South Africa Limited (AEC). Argonne National Laboratory (ANL) has begun a cooperation with one of these producers, CNEA, to convert their process to low-enriched uranium (LEU).

The CNEA process has been described in the literature [1] and has much in common with the Mallinckrodt process; both processes are based on that developed by A. Sameh [2]. In this process, the irradiated targets are heated in sodium hydroxide solution. The aluminum cladding and meat in the targets are dissolved to form sodium aluminate, and the uranium is precipitated, primarily as UO_2 . Molybdenum is soluble in alkaline solutions as the molybdate ion, but the actinides and many of the metallic fission-products precipitate as hydroxide salts. Following filtration of the dissolver solution, the filtrate is fed into an anion-exchange column, which retains molybdenum and some other anionic species. A series of separation processes purifies the molybdenum to meet pharmaceutical standards. As is common to all HEU processes we have studied, only the dissolution and primary molybdenum-recovery steps should be affected by conversion to LEU.

Early in 1999, ANL and CNEA began active cooperation with a goal to allow CNEA to convert to LEU at the end of three years. It is a multifaceted program with many steps. This paper will discuss only ANL progress. Tasks to be performed during 1999 are:

- Define loading and geometry of LEU targets and geometry of the irradiation rig (primarily a CNEA task). However, the schedule calls for ANL to provide the first LEU-metal-foil target for irradiation in the first quarter of 2000.
- Define LEU-target fabrication techniques (uranium-foil annular targets and high-density U-metal/Al-dispersion plates). Discussed below are some preliminary ANL efforts to fabricate a U-metal/Al-dispersion plate. The fabrication technique discussed in another paper in this session will be that used for a CNEA LEU-metal-foil target [3].
- Develop LEU-foil alkaline-digestion procedure. Argonne attempted two means of doing so: (1) dissolving the uranium foil in nitric acid and then precipitating the uranium with addition of base and (2) digesting the metal foil directly in alkaline solution at increased temperature and pressure.
- Study effects on the initial molybdenum-recovery step of the presence of zinc (and/or any other component changes) due to LEU-target conversion. Zinc is present in the LEU-metal-foil target as a fission-recoil barrier, which prevents bonding of the foil to the target walls during irradiation [4-6].

The following sections summarize our progress in these areas.

RESULTS

LEU-Foil Target

To yield equivalent amounts of ^{99}Mo , an LEU target must contain five times as much uranium as an HEU target. To keep the geometry the same as the HEU target, the LEU target requires a denser form of uranium. To that end, targets containing LEU in the form of a metal foil are being developed. A new annular-style target for irradiating LEU foils has been tested. The annular target is fabricated by sandwiching a piece of LEU foil between an inner and outer tube and then expanding the inner tube into the outer tube [3].

Currently, CNEA irradiates aluminum-clad uranium-alloy miniplates containing HEU for the production of ^{99}Mo . Since the new annular targets are cylindrical, they will not fit into CNEA's existing irradiation fixture. The CNEA staff has been working on designing a new irradiation fixture that will accommodate 4-6 annular targets. The irradiation fixture will maintain proper coolant velocities across the targets and will balance the flow between the inside and outside of the targets.

Each of CNEA's miniplates contains ~1.2 g HEU (1.1 g ^{235}U), and they can irradiate 1-8 plates in their current rig. The annular replacement target will be 36-mm OD and have a length of 145 mm (to fit into their existing transfer cask). A target with these dimensions can contain ~35 g LEU (7 g ^{235}U), assuming a 140- μm thick foil. Thus, the new annular target will allow

CNEA to increase their production capacity for ^{99}Mo . We have been working with them on the targets to ensure that the irradiation fixture and targets will be compatible. A new annular target will be fabricated and then shipped to CNEA during January 2000. This target is scheduled to be irradiated in March.

U-Metal/Al-Dispersion Targets

Conversion to LEU requires that the uranium loading in the current CNEA target be increased by five-fold. One means to do this in a plate-type target is to create a dispersion of uranium-metal powder in aluminum powder for fabrication. Uranium will react with aluminum in the meat during hot rolling. At full loading, the meat would be of pure UAl_x with no free uranium or aluminum. Preliminary activities were undertaken to test this concept. Aluminum-clad microplates of 20-25 vol% uranium-metal powder in aluminum powder were fabricated by a technique similar to that described for preparing advanced-fuel samples [7]. Fabrication parameters that were varied include:

- Uranium powder size (-100 mesh and +100 mesh)
- Uranium volume fraction (20 and 25 vol%)
- Rolling temperature (415 and 485°C)

Following preparation, physical and optical analyses were performed on the microplates.

In the first set of plates, a blister anneal was performed after hot rolling. The blister anneal gave the plate a surface relief "orange peel" texture over the fuel zones. To avoid the texturing effect, the blister-annealing step was eliminated for a second set of samples. All of the other parameters remained identical. No surface texture was noted on the plates without blister annealing. Bend testing to demonstrate cladding bonding resulted in no failures. Table 1 summarizes the reaction products and mixtures in the fuel zone for two microplates rolled at different temperatures.¹ Figure 1 shows the micrographs used to obtain these analyses. Results to date identify the effects of time and temperature on the reaction of uranium with aluminum in the fuel matrix. These initial studies indicate that it may be possible to fabricate acceptable U/Al-dispersion plates for irradiation for the low burn-up necessary (~1 %) for ^{99}Mo production. As expected uranium and aluminum in the fuel meat react during hot rolling, but the integrity of the plate was maintained; however, blister annealing should not be attempted.

Table 1. Optical Identification of U/AL phases for Microplates Rolled at Different Temperatures

Sample	Rolling Temp., °C ^a	Fraction of Micrograph Area Containing Metallurgical Phase, %				
		Al	90/10 ^b	58/42 ^b	32/68 ^b	UAl_3
A	485	32	-	28	28	12
B	415	30	25	-	-	45

^a Fuel contained 20 vol% of -100-mesh uranium powder.

^b Uranium/aluminum atomic ratio; these are not chemical phases but solid solutions of the metals and the chemical species UAl_2 , UAl_3 , and UAl_4 .

¹ For a 25-vol%-U plate that was hot rolled and blister annealed at 500°C for 2 hours, X-ray diffraction identified UAl_3 as the major phase. Minor phases also seen were UAl_2 , UO_2 , and aluminum; no metallic uranium was identified.

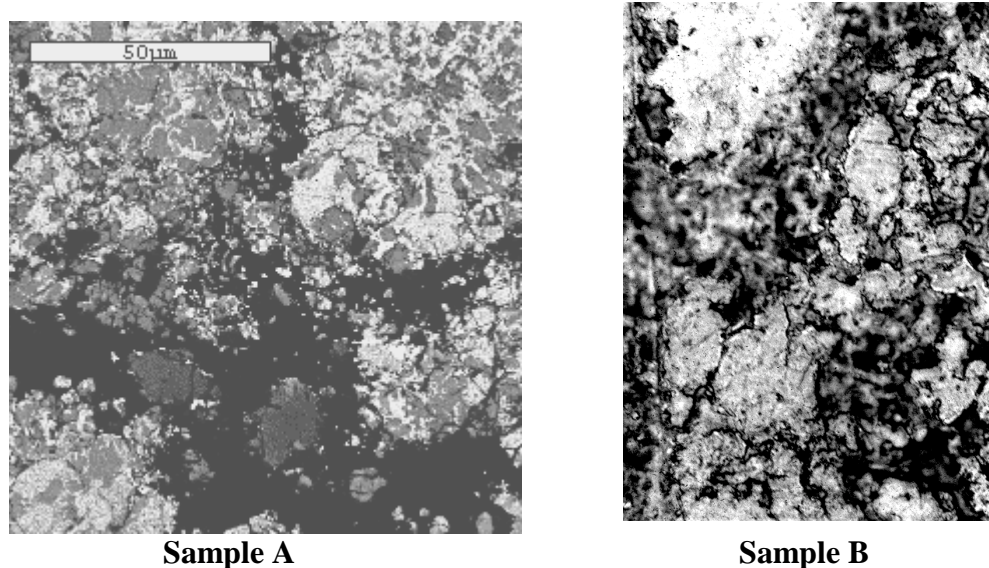


Fig. 1. Micrographs of the Fuel Meat for U/Al Dispersion Microplates Described in Table 1

Foil Dissolution/Digestion for ^{99}Mo Recovery

Because uranium metal dissolves very slowly in concentrated sodium-hydroxide solution at ambient pressure, alternative means are required for dissolving the target. Our development activities for uranium-foil digestion followed two parallel paths--(1) dissolution in nitric acid followed by making the dissolver solution basic with sodium hydroxide and (2) target digestion with alkaline solution under pressure, with or without O_2 present.

The CNEA now processes 5-9 g of HEU (93% ^{235}U) in one batch, so that a batch of about 25-50 g of LEU (<20% ^{235}U) must be used to produce the same quantity of ^{99}Mo . To avoid significant changes in the CNEA process, the feed to the initial molybdenum-recovery step must be alkaline. One method for this conversion is to dissolve the irradiated LEU foil in nitric acid, precipitate the uranium with sodium hydroxide, and filter or centrifuge the precipitate. The resulting solution can then enter the current CNEA process. The zinc added as a barrier material dissolves quickly in nitric acid and should have no effect on this step.

A series of experiments was run to look at a variety of process parameters, including initial uranium concentration, molybdenum concentration, temperature, digestion time, centrifugation vs. filtration, use and amount of filter aids, multiple washings of the precipitate, and multiple dissolving and precipitation steps. The bottom line in these studies is that precipitation of U(VI) from nitric acid solutions with sodium hydroxide is cumbersome. It produces sodium diuranate in the form of a voluminous, gelatinous precipitate. The precipitate contains a great deal of entrapped water, is difficult to filter without use of a filter aid, and is difficult to wash once it is compacted by either filtration or centrifugation. With that stated, the best conditions for fast, high recovery of soluble Mo(VI) in alkaline solution include the following:

- Dissolve the uranium-metal foil in nitric acid,
- Precipitate with the addition of 12 M NaOH and centrifuge the slurry,

- Decant the supernatant and dissolve the precipitate in nitric acid,
- Reprecipitate the U(VI) and centrifuge the slurry (for a total of three times), and
- Combine supernatants from all three decants) (this should contain >98% of the ^{99}Mo).

Results have shown that 45 g of uranium will produce a total volume of 750 mL with < 2% ^{99}Mo loss. Figure 2 plots the molybdenum loss for three initial concentrations of uranium under these conditions. The overall molybdenum yield increases with decreasing uranium concentration--from 98% (at an initial uranium concentration of 70 g/L) to 99.5% (at 10 or 30 g/L). These data show that ^{99}Mo loss can be reduced by increasing the solution volume and/or by performing an additional precipitation. Separation of the sodium diuranate by centrifugation is much simpler and faster than separation by filtration. This method should not take any more time to perform than the current HEU digestion.

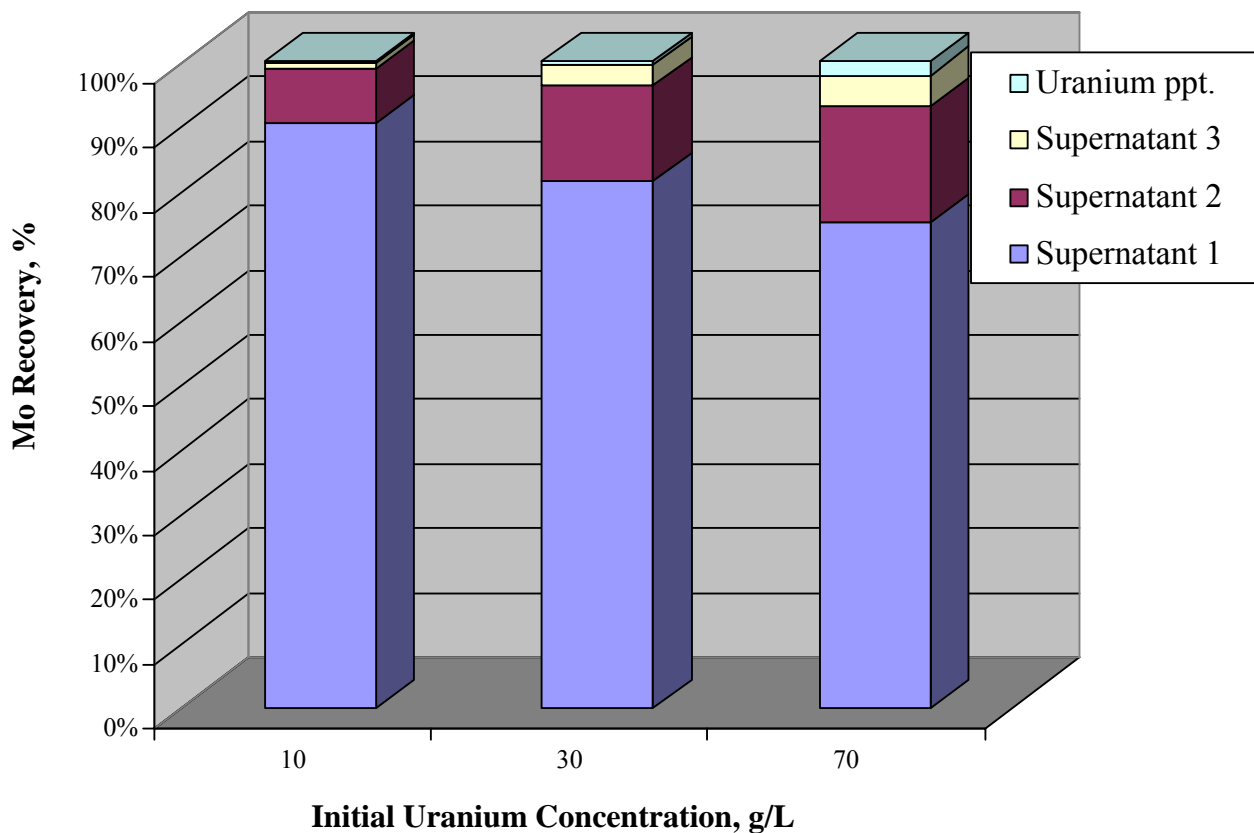


Fig. 2. Molybdenum Recovery from Nitric-Acid Dissolution of Uranium by Multiple Alkaline Precipitation and Acidic Dissolutions of U(VI)

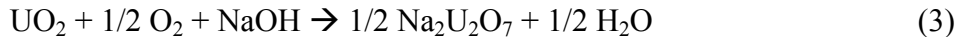
The feasibility of using a closed dissolver/digester to digest uranium foil in an alkaline solution was also studied. Since the uranium foil will be electroplated with zinc for alkaline-side dissolutions, experiments were performed with zinc foil alone, uranium foil alone, and zinc-plated uranium foils. Parameters studied were temperature (and therefore pressure),

dissolver solution composition (including concentrations of NaOH and NaNO₃), and addition of oxygen either as gas or in the form of the quickly decomposed H₂O₂. In this work, we used a Cintichem-type reusable dissolver developed for acid-side dissolution of uranium foil in a closed system. This closed dissolver can be operated at pressures up to 700 psig and at temperatures up to 225°C. The dissolver, which is flanged at one end so that the uranium foil can be loaded easily, was first described in 1995 [8]. An improved version, which was successfully tested by ANL and the Indonesian National Nuclear Energy Agency (BATAN), was described in 1998 [9].

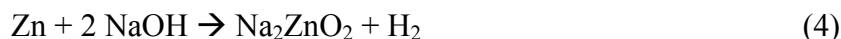
The major digestion and dissolution reactions in alkaline media are as follows. Uranium can be oxidized to U(IV) by reaction with water and/or oxygen to form UO₂:



The UO₂ can be further oxidized by oxygen to form sodium diuranate:



Zinc is dissolved in NaOH to give soluble sodium zincate:



We expected that nitrate would act as an oxidant in this system, but its addition had no effect on zinc dissolution and lowered uranium digestion rates. Oxygen addition did not increase uranium digestion rates, but its addition did change the final product to mostly Na₂U₂O₇.

Hydrogen gas was formed during digestion even with 100-psig-oxygen overpressure, presenting the safety concern of having significant amounts of hydrogen and oxygen gas in the same vessel. Therefore, neither nitrate nor oxygen will be used (or is required) for alkaline digestion of uranium.

The results to date are very encouraging. We have shown that zinc-plated uranium foils that are 5 mils (125 µm) thick or less can be digested in less than one hour. The digestions were done at 200°C in 1.0 to 2.5 M NaOH at mass-to-volume ratios (mass of U to volume of solution) up to 100 g/L. Thus, 50 g of U can be digested and the precipitate washed in far less than 500 mL of solution. The UO₂ particles are crystalline and filter easily. Likewise, the digestion rate has been shown to double every 18°C; therefore, thicker foils can also be digested in under an hour by increasing the digestion temperature.

Based on our results to date, we estimate that the required dissolver/digester for 50 g of Zn-plated uranium foil would have dimensions of 46-cm long by 5.7-cm diameter, and weigh about 3.6 kg. After digestion, the fission product gases can be removed with an adsorption pump (cold trap). The digester can be opened, and uranium particles separated from the solution by filtration. Following filtration of the solution from the uranium-containing precipitate, the solution, and any rinse solution, can then be processed to recover the ⁹⁹Mo in the normal fashion. The volume of the feed to the primary Mo-recovery step will be lower than that in the current HEU process, and the concentrations of aluminum and sodium will be greatly reduced.

Experimental results for both digestion paths were both positive; it is likely that either one could be made to work. However, alkaline digestion at elevated temperature/pressure would be far less complex and time-consuming. Future work will be limited to this path.

Primary Recovery of Molybdenum by Anion Exchange

A target with an LEU foil electroplated with a zinc fission-recoil barrier is the primary candidate for conversion of base-side processes. Therefore, it is necessary to study the separation behavior of zinc in the process for recovery and purification of ^{99}Mo . In the current CNEA process for HEU targets, anion exchange is employed for the primary separation of molybdenum [1]. In this step, molybdenum is adsorbed onto the anion-exchange resin, AG 1 X8, as molybdate ion from a 1.6–2 M NaOH solution. Zinc is soluble in alkaline media and will produce the hydrolyzed species $\text{Zn}(\text{OH})_4^{2-}$ and $\text{Zn}(\text{OH})_3^-$ in the dissolver solution. Because the concentration of zinc from foil digestion will be about 100 times higher than that of molybdenum produced by fission, the presence of zinc in the feed to the AG-1 column may interfere with the adsorption of MoO_4^{2-} . In this study, the adsorption behavior of Mo(VI) and Zn(II) from basic solution was examined.

The AG 1-X8 resin in chloride form was purchased from Bio-Rad Laboratories. All reagents were analytical or ACS-reagent grade. Radioactive isotopes, ^{99}Mo ($T_{1/2}=66\text{ h}$) and ^{65}Zn ($T_{1/2}=244\text{ d}$), were used as tracers. The conversion of the AG-1 resin to OH^- form was carried out using concentrated NaOH solutions. Typically, partitioning experiments were performed by contacting 1 g of resin with 10–12 mL of NaOH solution containing ^{99}Mo and/or ^{65}Zn . Contact was for 15 min with intermittent stirring. After settling, a portion of the solution was taken and gamma counted. The partitioning coefficient (K_D) for these experiments is the ratio of activity/g-solid and activity/mL-solution; its units are, therefore, mL/g. It is measured by counting the solution before and after contact and taking into account the material balance for the system. For column chromatography experiments, a small plastic column (0.8 x 4-cm, graduated) was used.

The effects of NaOH concentrations on the K_D values for sorption of ^{99}Mo and ^{65}Zn by the AG-1(OH) are shown in Fig. 3. At low concentrations of NaOH, $\leq 0.01\text{ M}$, the K_D values for both nuclides are higher than 1000. As $[\text{NaOH}]$ increases, K_D values for both radionuclides decrease; however, that for ^{65}Zn begins its decrease at lower $[\text{NaOH}]$. Therefore, the separation factor of Mo/Zn increases with $[\text{NaOH}]$ and reaches 100 at 1 M (Fig. 4). Based on these results, good separation of Mo(VI) from Zn(II) will be realized at 1.6–2 M NaOH.

The K_D values for both molybdenum and zinc are decreased by the presence of Cl^- or NO_3^- in solution. On the other hand, the presence of AlO_2^- had no effect on Mo(VI) sorption. Zinc at concentrations that correspond to the dissolver solution of the LEU-Zn target should not reduce the recovery of ^{99}Mo . At zinc concentrations from tracer up to 5 g/L, the K_D for ^{99}Mo was almost constant at 200–300 in 1 M NaOH solution, while the ^{65}Zn K_D varied from 3 to 4.

To confirm the separation of molybdenum from zinc, column chromatography experiments were carried out. Based on the current CNEA procedure [1], a 1.8 M NaOH feed and 1.0 M NaOH wash solutions were used. The elution curve for ^{65}Zn was flat during feed addition, the eluate containing essentially all the zinc contained in the feed. No ^{99}Mo was detected in the eluate samples; all was found in the resin phase after the elution.

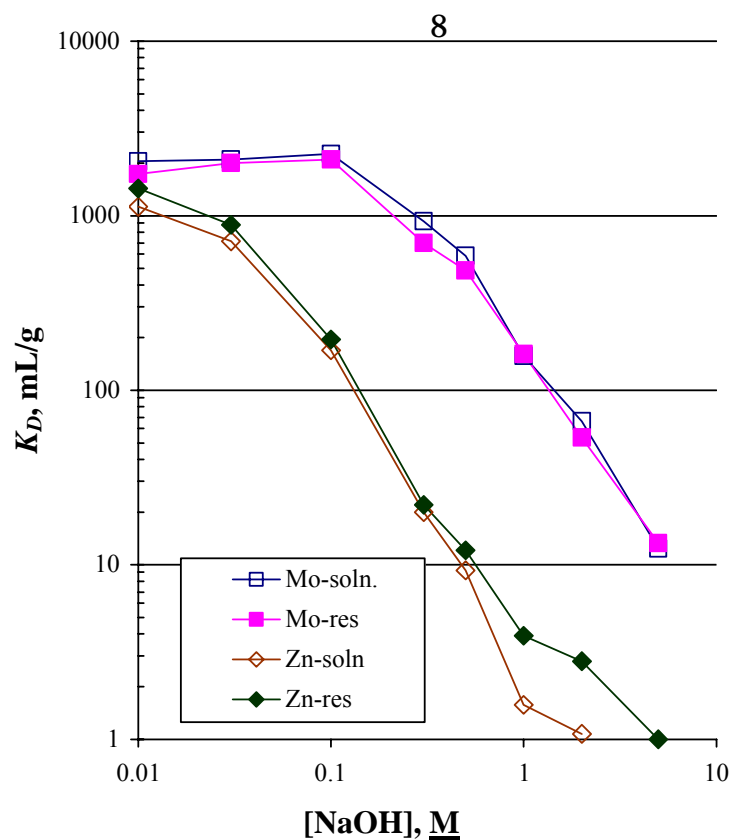


Fig. 3. Effects of Sodium Hydroxide Concentration on the K_D values for Molybdenum and Zinc for Sorption on AG-1 Resin. [K_D values were calculated by either difference in radioisotope activity in the solution before and after contact (soln) or by counting the resin directly (res).]

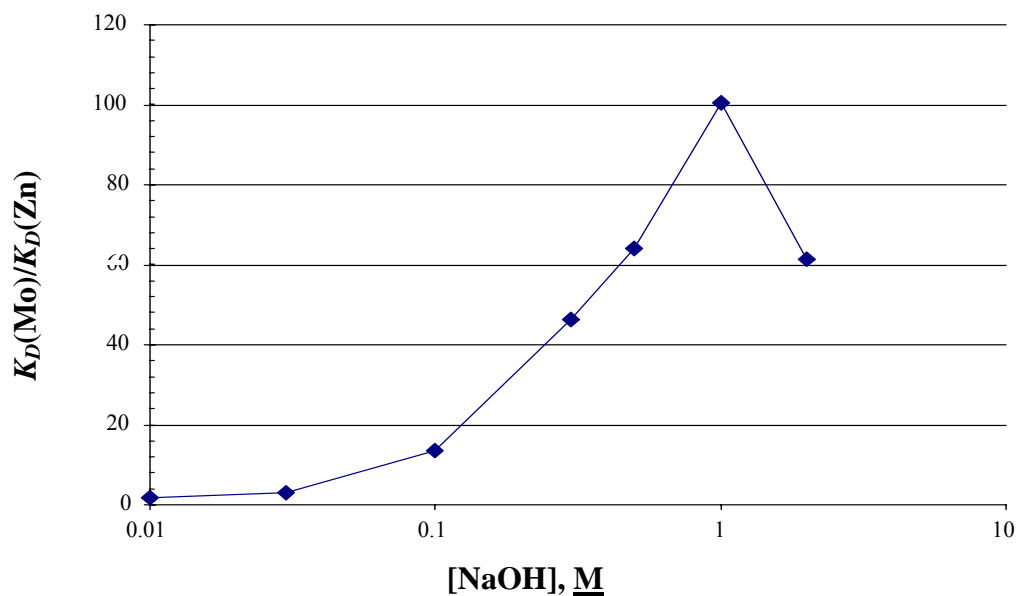


Fig. 4. Mo/Zn Separation Factor vs. NaOH Concentration

In the future, we will increase our knowledge of the important parameters in this primary molybdenum-recovery step and look at behavior of other anion exchange resins, including the microporous version of AG-1 (AG-MP) and Reillex HPQ. We will also increase the scope of our studies to include the recovery of molybdenum on alumina from acidic solution. This could be an alternative if the CNEA decides to take full advantage of conversion to LEU by modifying their current process.

CONCLUSIONS AND FUTURE WORK

The cooperation between ANL and CNEA is focused on allowing CNEA to convert ^{99}Mo production to LEU at the end of 2002. Both sides have active R&D underway in various aspects of the conversion. This paper has only discussed the ANL effort. Thus far, we have shown that:

- LEU metal-foil targets can replace the current HEU targets in the reactor and allow the same or more ^{235}U to be irradiated.
- LEU-metal/Al dispersion microplates have been fabricated and results are promising
- Zn-plated uranium foil can be digested in sodium hydroxide solution at a sufficient rate if done in a closed dissolver at elevated temperature. Another option, dissolving in nitric acid followed by precipitation of $\text{Na}_2\text{U}_2\text{O}_7$, can be made to work, but it would be more complex and time-consuming.
- Initial experiments suggest that the zinc fission-recoil barrier required on the LEU foil should not present a problem to the current processing scheme.

Future activities will move the process chemistry to CNEA hot cells and eventually to full LEU-process demonstrations. However, our current plan and schedule must be modified based on a recent CNEA decision to take full benefit of our conversion activities by modifying their current process to increase molybdenum yield and shorten processing time. They are investigating acidic dissolution of targets and use of alumina as a primary Mo-recovery step.

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